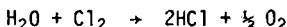


Ulrichson, Dean L. and Yu-Sung Yeh

Chemical Engineering Department and Ames Laboratory-ERDA
Iowa State University
Ames, Iowa 50011

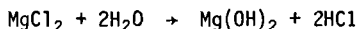
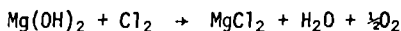
Introduction

A number of Thermochemical water splitting processes have been proposed which utilize the reverse Deacon Reaction to liberate oxygen from water. The balance of the process is devoted to liberating the hydrogen and regenerating chlorine and other reagents. The reverse Deacon reaction is a high temperature gas phase reaction.



The thermochemical data for this reaction are quite well documented and the free energy change is zero at about 860K. Proposals generally suggest running the reaction at 900 to 1200K with an excess of water to minimize the recycle of chlorine.

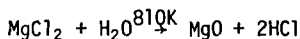
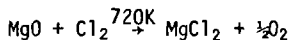
An alternate process for liberating oxygen is the pair of reactions involving magnesium compounds.



These reactions were proposed by Wentorf and Hanneman (1) of General Electric as part of one of their cycles. Note that the sum of these two reactions is the reverse Deacon reaction. Actually, these reactions are written as a condensed representation of the net effect of several reactions. The first reaction, as proposed at G. E., is run in aqueous solution and requires a catalyst to decompose an intermediate hypochlorite. Under the proper conditions nearly pure oxygen is evolved from the solution so that gas phase separation is minimized.

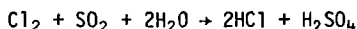
The second reaction in this pair is a high temperature solid-gas reaction which has been used commercially to produce MgO. One process which has been discussed in the literature (2) uses a spray tower for countercurrent contact of combustion products and water with MgCl₂. However, oxygen will react with HCl to regenerate chlorine, so the oxygen concentration in the combustion products must be minimized if HCl is the desired product.

A variant of this process is the use of both MgO and MgCl₂ in the solid phase as:

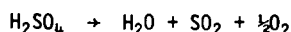


These reactions have been suggested by Abraham (3). The free energy change for these reactions is approximately zero at the indicated temperatures. The heat of reaction at 298K are -37.6kJ and 96.3kJ, respectively.

The list of alternates to the reverse Deacon reaction is essentially completed by mentioning the reactions suggested by Bowman (4):



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The first of these reactions would be a low temperature reaction producing concentrated sulfuric acid. The high temperature decomposition of sulfuric acid has been considered as part of several sulfur based thermochemical cycles. The sulfur reactions will not be considered further in this paper.

The purpose of this paper is to present preliminary kinetic data for each of these reaction schemes and compare processing requirements. Any of the above reaction paths could be used in a thermochemical cycle which requires the chemical effect of the reverse Deacon reaction. The choice among the processes depends upon the heat balance considerations, the work of separation and how well the process can be integrated with the rest of the cycle. Integration with a cycle is of primary importance in heat balance considerations and the recovery and reuse of HCl elsewhere in the cycle. That is, the need for a wet HCl gas, anhydrous HCl gas or aqueous solution of HCl may make one reaction scheme more attractive than another. Relative reaction rates and corrosion rates will also be important in terms of their affect on investment and maintenance costs.

Reverse Deacon Reaction

The thermochemical data for this reaction have been worked out and equilibrium compositions can be calculated reasonably accurately. Process heat balances have been reported (5) for the Mark 7 cycle and this, of course, includes the reverse Deacon reaction. The process diagram as proposed in that cycle is shown in Figure 1. Chlorine and water are fed to a reactor which operates at about 1000K. Assuming a stoichiometric feed mixture and equilibrium at the exit of the reactor, about 52% of the water and chlorine will be reacted and the HCl concentration will be about 46%. This means about 18 moles of HCl azeotrope will be circulated to the absorber for each mole of chlorine reacted. The absorber product will then be above the azeotrope composition and dry HCl can be taken from the top of the distillation column. The absorber offgas is then cooled to remove the remaining HCl and H₂O and the oxygen and chlorine are further cooled and compressed to separate liquid chlorine. The oxygen-chlorine compression work could be avoided by preferential absorption of chlorine in an appropriate solvent. One process has suggested sulfur monochloride as a solvent (6).

This process diagram has no provision for recovering the excess water which must be fed. Since each thermochemical cycle will have somewhat different needs for HCl and water, the best means for recycling the water will vary. Obviously, some water could be recycled from the absorber offgas condenser. The other possibility is installation of an azeotrope breaker column in the azeotrope recycle stream. Sulfuric acid is frequently used to dry an HCl-H₂O azeotrope. For purposes of comparing the reverse Deacon process with alternate processes, the recovery of the water and the source and composition of the HCl stream to be used in the thermochemical cycle are not primary consideration. That is, comparison of the oxygen liberating processes will not depend heavily on the recovery and recycle of water since most processes will have similar needs.

The kinetics of this reaction have received very little attention. Scattered literature results indicate that the uncatalyzed rate of reaction is quite slow. Catalysts for the Deacon reaction, the reverse of the reaction used here, have been developed but they are too volatile for the projected operating temperature. A patent assigned to Air Reduction Co. (6) suggests using rare earth chlorides which would seem to be reasonable. Russian workers (7) have used mixtures of MgO, MgCl and CaO as catalysts, but volatility may also be a problem with these compounds. None of these workers have presented reaction rate data. Therefore, it is not known whether a catalyst will be required at the proposed operating temperature of 1000K.

To obtain preliminary reaction rate data on the reverse Deacon reaction, a simple once-through system was assembled as a plug flow reactor. The chlorine and steam feed streams were preheated and passed through a mixing zone prior to entering

the reactor. The reactor temperature was maintained by a clamshell furnace controlled to $\pm 3^\circ\text{C}$. The reactor was constructed of 6mm ID Vycor tubing about 150cm long. The reactor was constructed in five horizontal passes through the 30cm furnace. This construction was necessary to provide an adequate velocity in the reactor while obtaining sufficient residence time to give 10 to 20% conversion. The progress of the reaction was monitored by condensing H_2O and HCl in a water scrubber, reacting excess Cl_2 in a KI solution and finally collecting the O_2 in an inverted graduated cylinder. The chlorine and water flow rates were varied in each run so that the residence time in the reactor varied between 2.5 and 6.5 seconds while the ratio of water to chlorine feed concentration varied between 0.5 and 2.0.

The experiments were run at atmospheric pressure and two temperatures, 900K and 950K. The results are given in Table 1. These data were analyzed by assuming a rate equation and applying the plug flow reactor model. The general rate equation

$$r = k_1 \{\text{Cl}_2\}^a \{\text{H}_2\text{O}\}^b - k_2 \{\text{HCl}\}^c \{\text{O}_2\}^d \quad (1)$$

was used where the brackets indicate concentrations in moles per liter. Since the equilibrium conversions for this reaction are greater than 40% and the measured conversions were always less than 50% of the equilibrium conversion, the reverse reaction was considered negligible. All integer combinations of a and b between 0 and 2 were used to test rate models. Values of $a=\frac{1}{2}$ with $b=0$ or 1 were also tried. A total of 12 reaction rate models were tested.

The plug flow reactor model (see e.g., 8) in the form was used to test each

$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{r} \quad (2)$$

rate equation. By defining X_A as the moles of chlorine reacted per mole of chlorine fed and accounting for the volume change with extent of reaction, the concentration of chlorine is $(\text{Cl}_2) = C_A = C_{A0} \frac{(1-X_A)^{2(N+1)}}{2(N+1)+X_A}$. Here, C_{A0} is the feed concentration

in g-moles/liter. Using these concentrations in equation 1 with $k_2=0$, substituting equation 1 into equation 2 and integrating relates the reactor exit conversion, X_{Af} , to the residence time τ and the molar water to chlorine feed ratio, N .

The model which appears to give the best fit results from using $a=1, b=0$ in equation 1. The result in this case is

$$k_1 \tau = - \frac{X_{Af} + (2N+3) \ln(1-X_{Af})}{2N+2} = X \quad (3)$$

A plot of the right hand side of equation 3 versus τ will give a straight line of slope k_1 if the correct rate equation has been chosen. A plot of equation 3 is shown in Figure 2 for both the 900K and 950K experiments. The values of k_1 , are 0.032 sec^{-1} at 900K and 0.051 sec^{-1} at 950K. Assuming an Arrhenius relationship, $k_1 A e^{-E/RT}$, gives $A=224 \text{ sec}^{-1}$ and $E=66.2 \text{ kJ}$.

All 12 rate expressions were similarly analyzed. With one exception, none of the other rates expressions approximated a linear relationship. The exception is the case of $a=2, b=1$ or $r=k_2(\text{Cl}_2)^2(\text{H}_2\text{O})$ 4). Figure 3 shows the results for equation 4 when plotted in the manner corresponding to equation 3. The straight lines in Figure 3 yield the constants $k_2=880 (\text{g-mole/l})^{-2} \text{ sec}^{-1}$ at 900K, $k_2=1762 (\text{g-mole/l})^{-2} \text{ sec}^{-1}$ at 950K, $E=971. \text{ kJ}$ and $A=3.82 \times 10^6$.

The model shown in Figure 2 appears to give a slightly better fit of the data than the one in Figure 3, particularly at 950K. This model is also easier to justify mechanistically in that it implies that the reaction which forms chlorine radicals is

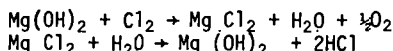


rate controlling. The slightly greater dispersion of the data at 950K might suggest that the formation of chlorine radicals is not the only rate limitation at the higher temperature. In any event it seems obvious that these data should be used only in the range of conditions under which they were determined.

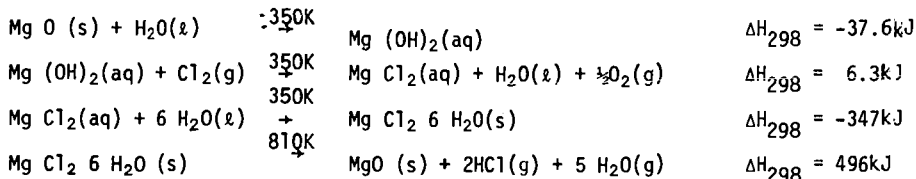
The residence time required here suggests that a catalyst would be justified to increase the reaction rate (decrease the residence time) in a commercial scale reactor operating at 900 to 950K. In that case, cooling of the reactor products would probably be rapid enough to avoid a significant amount of reverse reaction. If the reaction temperature is raised to 1100K, a catalyst may not be necessary but the initial cooling would need to be very rapid to avoid the reverse reaction. Further data are required to clarify this point.

Mg(OH)₂ - MgCl₂ Reactions

The magnesium reactions proposed by Wentorf and Hanneman (1) of General Electric were written as



Although they recognized that these reactions were not the reactions that actually occurred, they did not indicate all the potential difficulties. A more indicative, but still incomplete, reaction sequence can be written as

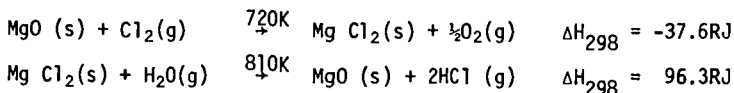


All of these reactions occur quite readily. The second reaction produces an intermediate hypochlorite which must be decomposed catalytically. The addition of cobalt chloride, for example, produces a finely divided cobalt oxide which permits the hypochlorite decomposition to proceed very rapidly (9). However, this reaction will not occur in a concentrated MgCl₂ solution. Therefore, reaction 2 must be run in a dilute solution and the excess water must then be evaporated to crystallize MgCl₂·6 H₂O in reaction 3. This evaporation adds substantially to the already excessive heat load for the process. The crystallization process will also remove the catalyst from solution and the catalyst would then pass through reaction 4. However, when the cobalt oxide catalyst is removed from solution and dried it becomes a less effective catalyst. Some catalyst regeneration procedure would probably be required to provide finely divided particles again for reaction 2.

The catalyst handling problems, the concentration and crystallization of MgCl₂ from solution and the excessive heat required to decompose the hexahydrate to MgO are each serious detriments to this process and collectively, preclude further consideration of this process as an alternate to the reverse Deacon reaction.

MgO-MgCl₂ Reactions

The catalyst and dehydration problems of the above reactions can be avoided by running solid-gas reactions written as



magnesium compounds on a porous surface and alternately passing steam and chlorine over the bed. The use of two beds in much the same way as ion exchange resins are used would provide a semi-continuous process. The data presently available indicates that no other process using the magnesium reactions is an alternative to the reverse Deacon reaction.

Conclusions

The reverse Deacon reaction is shown to require very high temperatures (1100K or higher) or a catalyst to obtain satisfactory reaction rates. If a high temperature is used, the reverse reaction is likely to occur as the products are cooled. The reverse reaction could be minimized by very rapid cooling but this would incur irreversible heat losses in addition to the heat required to drive the reaction. The work of separation and recycle is also very large for this reaction.

Preliminary experimental work on the chlorination of magnesia and the hydrolysis of magnesium chloride indicates that both these reactions must be run as solid gas reactions. In addition, they must be run in such a way that diffusional limitations to the reaction rate are avoided. Successful demonstration of such a process may lead to a good alternate to the reverse Deacon reaction.

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Translated for Ames Laboratory, ERDA.

Table 1
Experimental Results

Run Number	Feed Rate* (c.c./min)	$(\text{Cl}_2) \times 10^3$ (g-moles/l)	$(\text{H}_2\text{O}) \times 10^3$ (g-moles/l)	N	τ (Sec.)	Conversion (%)
A 1	847	5.823	7.727	1.327	2.41	6.91
A 2	725	4.523	9.027	1.996	2.81	7.88
A 3	847	5.823	7.727	1.327	2.41	6.91
A 4	725	4.523	9.027	1.996	2.81	7.06
A 5	550	6.559	6.991	1.066	3.71	9.24
A 6	611	7.258	6.292	0.867	3.34	8.16
A 7	550	6.559	6.991	1.066	3.71	9.24
A 8	611	7.258	6.292	0.867	3.34	8.20
A 9	780	6.327	7.223	1.141	2.62	8.34
A 10	658	4.987	8.563	1.717	3.10	10.77
A 11	780	6.327	7.223	1.141	2.62	8.31
A 12	658	4.987	8.563	1.717	3.10	10.59
A 13	463	4.523	9.028	1.996	4.41	13.82
A 14	495	5.108	8.442	1.653	4.12	14.29
A 15	532	5.691	7.859	1.381	3.84	14.13
A 16	574	6.276	7.274	1.159	3.55	13.60
A 17	636	6.976	6.574	0.942	3.21	12.06
A 18	550	5.958	7.592	1.274	3.71	13.62
A 19	471	4.450	9.102	2.046	4.33	9.48
A 20	503	5.030	8.520	1.694	4.06	11.87
A 21	539	5.610	7.941	1.416	3.78	11.20
A 22	582	6.193	7.357	1.188	3.50	12.38
A 23	643	6.893	6.657	0.966	3.17	10.81
A 24	313	6.695	6.855	1.024	6.52	17.50
A 25	345	7.333	6.217	0.848	5.92	16.90
A 26	382	7.931	5.619	0.708	5.35	14.76
A 27	424	8.498	5.052	0.594	4.81	13.46
A 28	486	9.135	4.415	0.483	4.20	12.12
B 1	332	6.365	6.472	1.017	6.14	21.96
B 2	364	6.938	5.898	0.850	5.60	23.28
B 3	403	7.505	5.332	0.710	5.06	24.00
B 4	448	8.043	4.794	0.596	4.55	23.15
B 5	513	9.127	4.423	0.485	3.98	21.15
B 6	398	5.317	7.520	1.414	5.13	19.61
B 7	430	5.882	6.955	1.182	4.74	20.33
B 8	469	6.457	6.380	0.988	4.35	20.55
B 9	514	7.018	5.819	0.829	3.97	20.23
B 10	579	7.668	5.169	0.674	3.52	17.94
B 11	441	4.792	8.044	1.678	4.62	18.69
B 12	474	5.341	7.496	1.403	4.31	20.22
B 13	512	5.908	6.928	1.173	3.98	18.54
B 14	558	6.470	6.366	0.984	3.66	17.24
B 15	622	7.132	5.705	0.800	3.28	15.64
B 16	479	4.412	8.424	1.909	4.26	19.87
B 17	512	4.944	7.892	1.596	3.99	19.89
B 18	550	5.500	7.336	1.334	3.71	19.27
B 19	596	6.058	6.779	1.119	3.42	18.54
B 20	660	6.721	6.116	0.910	3.09	16.14

*A-Group are based on 900°K

B-Group are based on 950°K

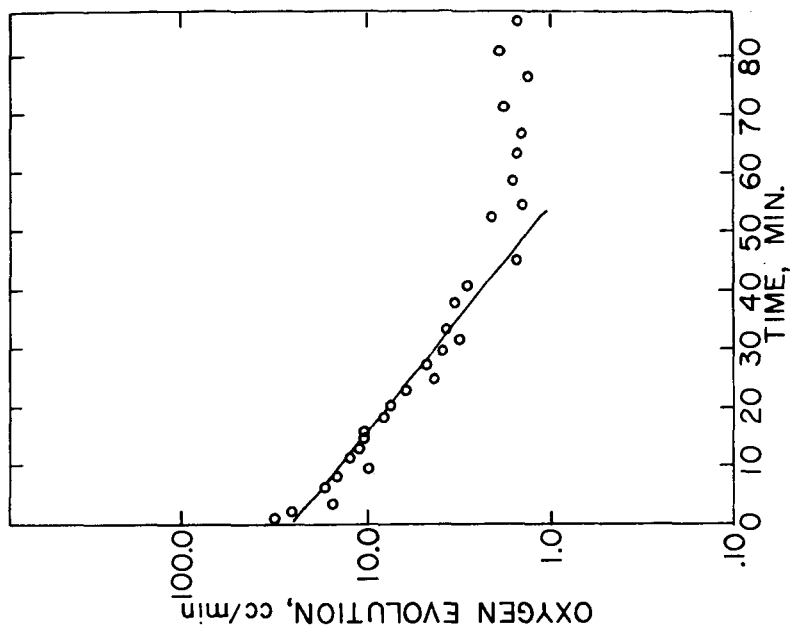


Figure 5

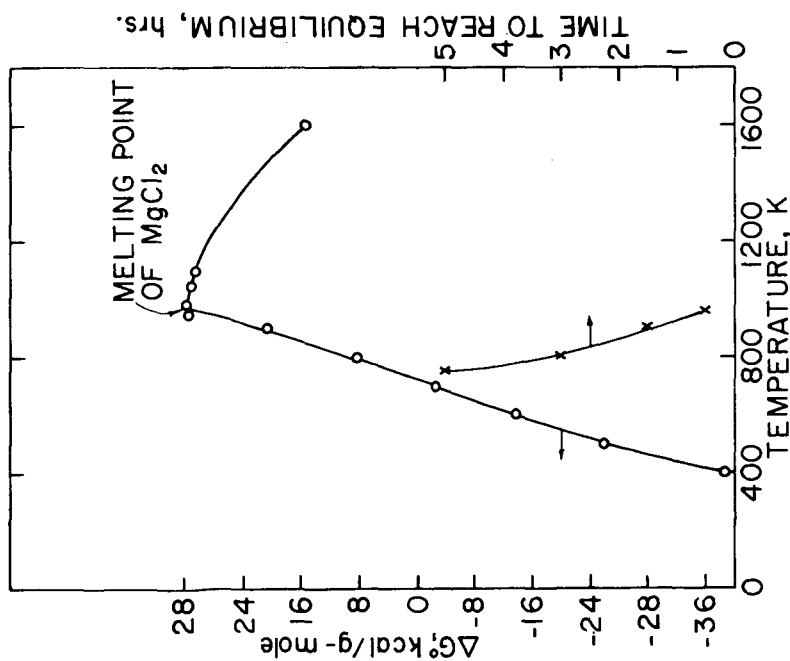


Figure 4